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Anhydrous $ZnCl_2$ Catalyzed Synthesis of 2–Aryl Substituted Benzimidazole Derivatives

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Abstract

Anhydrous $ZnCl_2$ was used to be a catalyst for the synthesis of 2-arylsubstituted benzimidazoles efficiently. In this method is very simple convenient procedure, easy purification and shorter reaction time. So we prepared the many benzimidazole derivatives from this method. All the synthesized compounds were characterized melting point, IR, ^1H NMR, ^{13}C NMR spectral data conformed the structure of the newly synthesized compounds.

Keywords: *Anhydrous $ZnCl_2$; Chromatography; o-phenylenediamine benzimidazole; Spectroscopy.*

1. INTRODUCTION

Benzimidazole is one of the important heterocyclic groups manifesting various biological properties such as antibacterical, antifungal and antihelmintic activities. Compound containing benzimidazole ring which are formed via the fusion of imidazole and benzene ring, have been used extensively for pharmaceutical purposes since 1960 (Buu-Hoi *et al.* 1963). Benzimidazole derivatives exhibit significant activity against several viruses such as HIV (Jones *et al.* 1990) herpes (HSV-1) (Grimmet, 1996), RNA (Preston, 1980), influenza (Kanazawa *et al.* 2006) and human cytomegalovirus (HCMV).The widespread interest in benzimidazoles - containing structure has promoted. In recent times we have shown $KHSO_4$ and p-TSOH can be used as promoters and catalysts for the synthesis of benzimidazole (Gracias *et al.* 2005; Tamm *et al.* 1978; Siddiqui, *et al.* 2005). So we tried to synthesis benzimidazole using inorganic catalyst. In this paper anhydrous $ZnCl_2$ was used for the synthesis of 2-arylsubstituted benzimidazole by the condensation of aryl aldehyde with *o*-phenylenediamine.

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2. EXPERIMENTAL SECTION

2.1 General Procedure

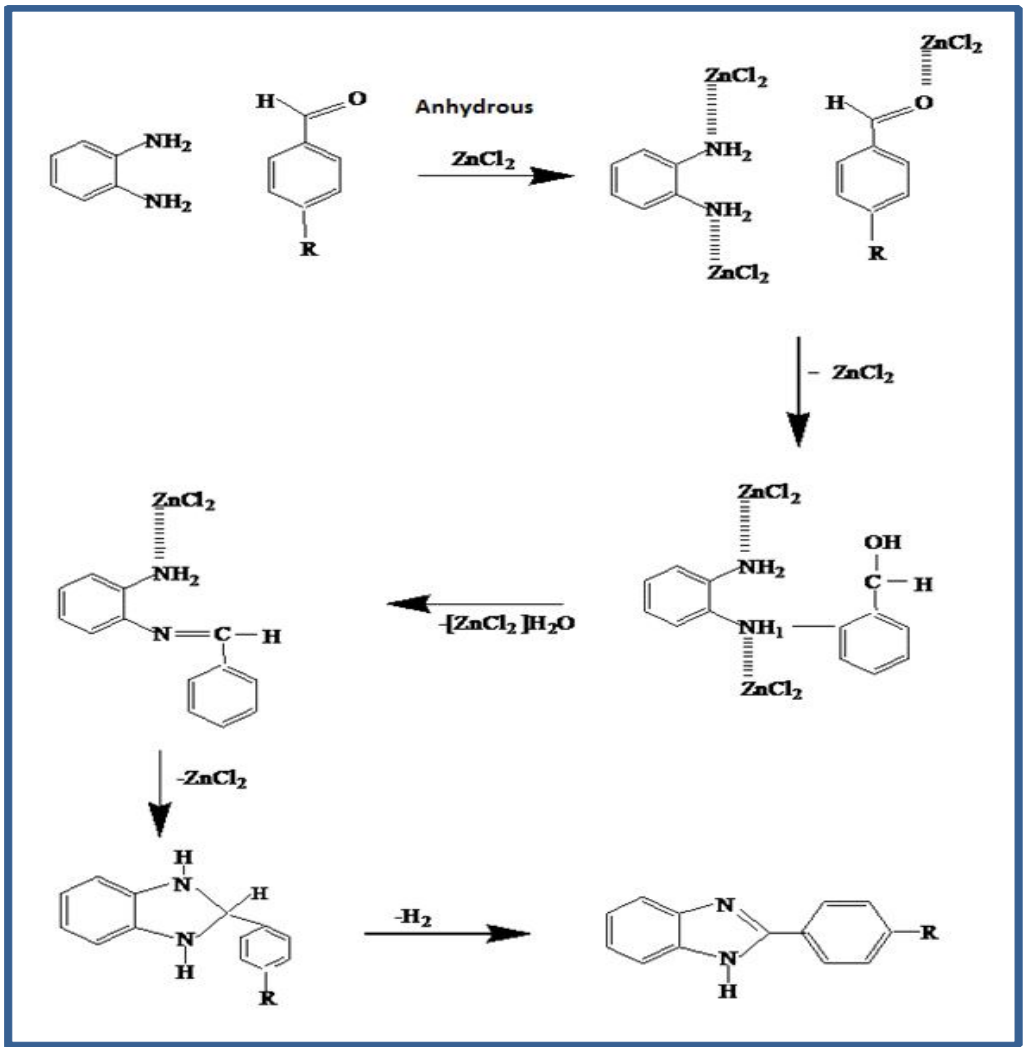
All melting points were determined on a kofler micro melting point apparatus and were uncorrected. IR spectra were recorded on a Perkin Elmer spectrophotometer using KBr pellet method. ^1H NMR and ^{13}C NMR spectra were measured on a Bruker spectrophotometer using TMS as internal standard. Typical procedure for synthesis of benzimidazole.

3. RESULT & DISCUSSION

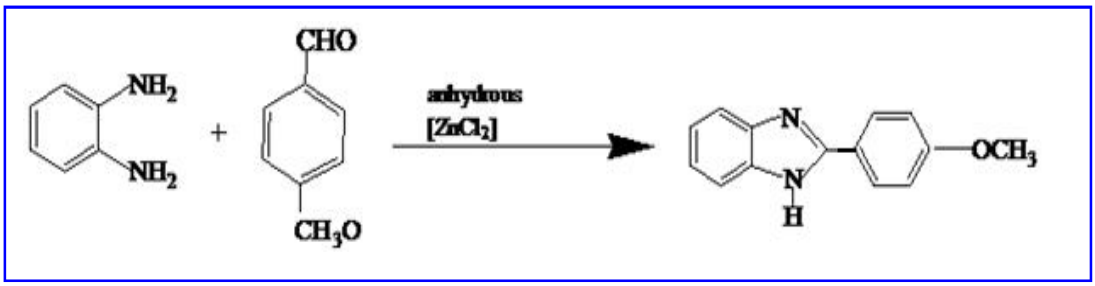
Anhydrous zinc chloride hydrolyzes with moisture to form hydrochloric acid. It also forms complex ions with water, ammonia and some organic solvents. Alkaline materials precipitate zinc hydroxide from zinc chloride solutions. Zinc laurate, linoleate or resinate can be formed from zinc chloride solutions and solutions of

the corresponding sodium salt. Zinc chloride is a Lewis acid and therefore electrophilic in character. Its catalytic activity is milder than that of aluminium chloride in, for example, Friedel-Crafts type reactions. Zinc chloride is particularly effective in catalyzing reactions that eliminate molecules of water, ammonia or mercaptans. As a part of our ongoing investigation as developing versatile and efficient method for synthesis of heterocyclic compounds. We discussed here synthetic method of benzimidazoles form aldehydes and *O* – phenylenediamine in presence of anhydrous $ZnCl_2$.

One pot synthesis of benzimidazoles regarding the mechanism of the step is proposed given below,

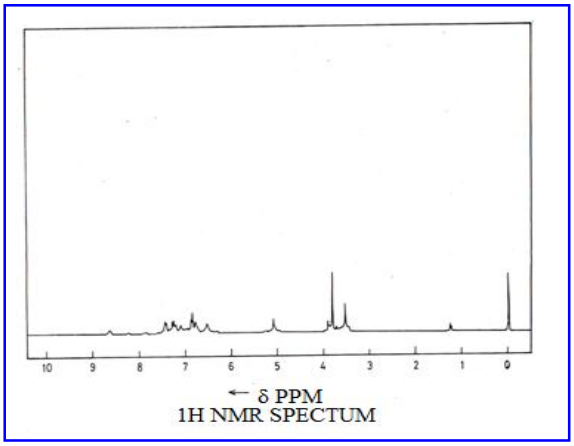


4. REACTION OF O-PHENYLENEDIAMINE WITH ANISALDEHYDE IN PRESENCE OF ANHYDROUS

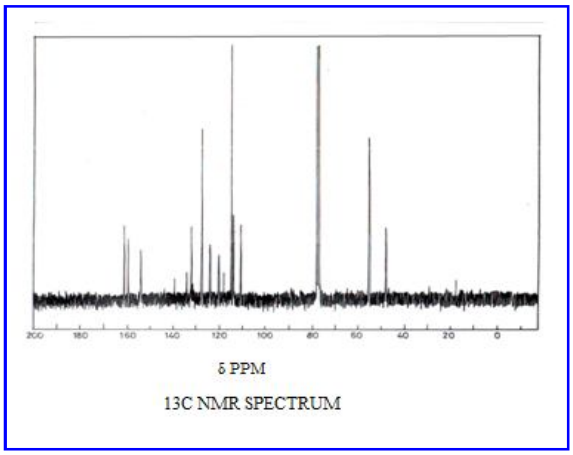


4.1 1H NMR - Spectral Data of compound

Proton	Signal (ppm)
H – 2',6'	7.6(dd,2H)
H – 3',5'	7.22(m,1H)
H – 4'	6.82(m,1H)
H – 3',5'	7.32(m,1H)
H – 4	6.62(m,1H)
H – 5	7(m,1H)
H – 6	7.45(m,2H)
H – 7	7.42 (m,2H)
N – H	5.10(6rs, 1H)
OCH_3	3.82(m,3H)



1H NMR SPECTUM

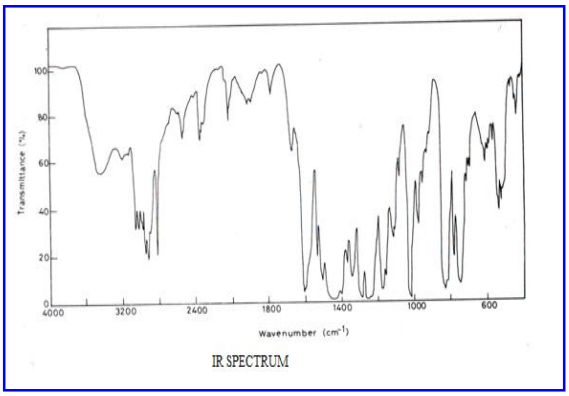


13C NMR SPECTRUM

Carbon	Signal (ppm)
C – 2	155.5
C – 4	119.924
C – 5	127.174
C – 6	130.97
C – 7	110.71
C – 8	133.82
C – 9	139.28
C – 1'	130.97
C – 2'	131.74
C – 3'	123.93
C – 4'	127.17
C – 5'	126.8
C – 6'	131.92
OCH_3	55.32

^{13}C NMR Spectral Data of the Compound

All the carbon signals are in between δ 100 – 155 suggesting only aromatic and unsaturated carbon atom are present. Out of 16 carbon signals four signals δ 155.5, δ 130.97, δ 139.28 and δ 133.82 are weak intensity showing the presence four quaternary carbon atoms.



IR SPECTRUM

4. IR spectral data of compound

In IR spectral data of compound was exhibits an absorption of 3217.04 N- H starching, 1605.43 for C=C 1302 for C – N group.

5. CONCLUSION

We have developed a simple one pot synthesis of 2-aryl substituted benzimidazoles by the condensation of o-phenylenediamine with aryl aldehydes catalyzed by anhydrous $ZnCl_2$. The simplicity of the reaction condition pot with shorter reaction time and with column chromatography to get the pure product. Simple and convenient procedure, easy purification shorter reaction time, and very good yield are the advantageous features of these methods and we have finished the spectral studies of IR ^{1}H NMR, ^{13}C NMR of spectral data confirmed the structure of the newly synthesized compounds.

REFERENCES

Jones, R. C. F. and Nichols, J. R., Thiamineco enzyme models: Imidazoliniumylides and there actions of 2-(hydroxyalkyl) imidazolines, *Tetrahedron Lett.*, 31, 1771–1774 (1990).http://dx.doi.org/10.1016/S0040-4039(00)88877-2

Grimmet, M. R., A. R. Katcizky, C. W., Ress, E. F. and Sriven, Comprehensive Heterocyclic chemistry, Edn. Pergamon, Oxford, 3, 77 (1996).

Preston, P. N. and Stevens, M. F. G., Benzimidazoles and congeneric Tricyclic compounds Part2, JohnWiley & Sons, NewYork, 1980.

Kanazawa, C., Kamijo, S. and Yamamoto, Y., Synthesis of Imidazoles through the Copper-Catalyzed Cross-Cyclo addition between Two Different Isocyanides, *J. Am. Chem., Soc.*, 128, 10662–10663 (2006).http://dx.doi.org/10.1021/ja0617439

Gracias, V., Gasiecki, A. F. S. and Djuric, W., Synthesis of Fused Bicyclic Imidazoles by Sequential Van Leusen/ Ring-Closing Meta thesis Reactions, *organic lett.*, 7, 3183–3186 (2005).http://dx.doi.org/10.1021/ol050852

Siddiqui, S. A., Narkhede, U. C., Palimkar, S. S., Daniel, T., Lahoti, R. J., Srinivasan, K. V., Room temperature ionic liquid promote di-mproved and rapid synthesis of 2,4,5-triaryl imidazoles from aryl aldehydes and 1,2-diketones or á-hydroxyketone, *Tetrahedron.*, 61, 3539-3546 (2005).http://dx.doi.org/10.1016/j.tet.2005.01.116

Tamm, I. and Sehgal, P. B., Halobenzimidazoleribosides and RNA synthesis of cells and viruses, *Adv. Virus Res.*, 22187–258 (1978).http://dx.doi.org/10.1016/S0065-3527(08)60775-7